



# Capping with activated carbon reduces nutrient fluxes, denitrification and meiofauna in contaminated sediments

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## ABSTRACT

Sediment capping with activated carbon (AC) is an effective technique used in remediation of contaminated sediments, but the ecological effects on benthic microbial activity and meiofauna communities have been largely neglected. This study presents results from a 4-week experiment investigating the influence of two powdered AC materials (bituminous coal-based and coconut shell-derived) and one control material (clay) on biogeochemical processes and meiofauna in contaminated sediments. Capping with AC induced a 62–63% decrease in denitrification and a 66–87% decrease in dissimilatory nitrate reduction to ammonium (DNRA). Sediment porewater pH increased from 7.1 to 9.0 and 9.7 after addition of bituminous AC and biomass-derived AC, respectively. High pH (>8) persisted for at least two weeks in the bituminous AC and for at least 24 days in the coconut based AC, while capping with clay had no effect on pH. We observed a strong impact (nitrate fluxes being halved in presence of AC) on nitrification activity as nitrifiers are sensitive to high pH. This partly explains the significant decrease in nitrate reduction rates since denitrification was almost entirely coupled to nitrification. Total benthic metabolism estimated by sediment oxygen uptake was reduced by 30 and 43% in presence of bituminous coal-based AC and coconut shell-derived AC, respectively. Meiofauna abundances decreased by 60–62% in the AC treatments. Taken together, these observations suggest that AC amendments deplete natural organic carbon, intended as food, to heterotrophic benthic communities. Phosphate efflux was 91% lower in presence of bituminous AC compared to untreated sediment probably due to its content of aluminum (Al) oxides, which have high affinity for phosphate. This study demonstrates that capping with powdered AC produces significant effects on benthic biogeochemical fluxes, microbial processes and meiofauna abundances, which are likely due to an increase in porewater pH and to the sequestration of natural, sedimentary organic matter by AC particles.

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## 1. Introduction

Sediments represent the largest ecosystem on Earth in spatial coverage and metabolize large amounts of settling organic matter and pollutants through the activity of living benthic macro- and microorganisms (Atlas, 1981; Middelburg et al., 1993). Thermodynamically, oxygen and nitrate are the most valuable electron acceptors for organic matter degradation (Canfield et al., 2005). Most

of benthic microbes are thus confined to surface sediments, where oxygen and nitrate are available and organic matter quality and quantity peaks. Inorganic compounds such as nitrate, ammonium, phosphate and silicate are products of microbial degradation of organic matter and may be either sequestered in the sediment by geochemical processes, or be released to the water column and assimilated as nutrients by microorganisms and primary producers and be retained in the food web.

Benthic invertebrates also play a primary role in the transformation of organic matter and in the mobilization of solutes in the sediment through bioturbation and bioirrigation (Aller and Aller, 1992; Kristensen, 2000; Nascimento et al., 2012). Meiofauna, i.e., invertebrates with dimensions between 40 µm and

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1 mm, are the most abundant and diverse group of benthic metazoans (Rex et al., 2006). Despite their abundance and richness, the functional role of meiofauna in marine ecosystem has been overlooked, as most studies have prioritized the investigation of macrofauna, i.e., invertebrates larger than 1 mm. However, meiofauna have recently been shown to mediate vital ecosystem functions such as the degradation of organic matter (Nascimento et al., 2012) and denitrification (Bonaglia et al., 2014b) in aquatic sediments.

Marine sediments are major repositories for metals and persistent organic pollutants (POPs) derived from human activities. These pollutants include dioxins, polychlorinated biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs). Environmental contamination by POPs and metals may be toxic to marine life and also impact important geochemical processes mediated by specialized microbes, and thus compromise the natural recovery capacity of the ecosystems (Islam and Tanaka, 2004). Remediation of human-origin pollution is becoming a necessity in order to decrease ecological and human health risks and to meet sediment quality criteria. Remediation techniques generally consist in monitored natural recovery, dredging (mechanical removal of contaminated sediment) or capping (sediment isolation through covering with clean materials) (Förstner and Apte, 2007). Dredging is expensive and time-consuming, it completely removes benthic biota, and may negatively affect water quality (Fathollahzadeh et al., 2015). Classic isolation techniques with geo-textiles and thick-layer caps are also highly disruptive and associated with high costs. As such, researchers have in the last two decades focused on less expensive and less invasive thin-layer capping techniques utilizing sorbent materials and especially activated carbon (AC) (Choi et al., 2016; Ghosh et al., 2011; Perelo, 2010).

Source material for activated carbon can be derived either from coals such as bitumen or anthracite or from natural biomass (e.g., wood, seeds, fruit shells). These materials undergo pyrolysis and are chemically activated to enhance their surface-to-volume ratio (Marsh and Reinoso, 2006) and thus their reactivity. The greater efficiency of powdered compared to granular AC is related to the higher probability for a diffusing contaminant to interact with powdered forms, as the average distance between powder particles is much lower than that of granular materials in the media, thus increasing the probability and rate of interactions (Zimmerman et al., 2005). The efficiency of the AC materials to bind pollutants is thus inversely proportional to their particle size (Werner et al., 2006; Zimmerman et al., 2005). However, at longer time scales (e.g., decades), the effect of particle size becomes less apparent as sorption equilibrium will be approached (Werner et al., 2006).

Recent research into sediment remediation has found that AC may cause secondary negative effects on benthic organisms. Two recent studies following AC capping efforts *in situ* demonstrated that macrofauna living in the sediment was drastically reduced (Cornelissen et al., 2011; Samuelsson et al., 2015). Slightly larger particle sizes are usually advised for sediment remediation applications because they induce less secondary effects compared to finer AC particles (Janssen and Beckingham, 2013). Negative effects of powdered AC on macro-benthic invertebrates have been observed in several studies and include decreased survival rates, growth rates, and lipid content, as well as behavioral changes (Abel et al., 2017; Janssen and Beckingham, 2013; Näslund et al., 2012; Nybom et al. 2015, 2016). Capping with sediment (clay) is expected to produce less ecological impacts than AC capping but, in case of remediation treatments, this should be weighed against its low efficiency in reducing POP fluxes specifically from bioturbated sediments (Lin et al., 2018).

The effects of AC amendment on sediment microorganisms and meiofauna remain lesser-known. Apparently, adsorption of PCBs by granular AC seems to affect bacterial transformation of PCBs in

sediments (Kjellerup et al., 2014), but no detrimental AC effects were observed on bacterial community structure and functions in contaminated soil (Meynet et al., 2012). Only one study so far has addressed the impact of thin-layer capping on bacterial production and community composition in sediments, but potential mechanisms causing secondary effects were not addressed (Näslund et al., 2012). Thermally activated carbonaceous materials have been shown to potentially raise the pH of solutions by one to three units (Mohan and Pittman Jr., 2006), dependent on *in situ* water chemistry. The effects of thin-layer capping on pH needs therefore to be evaluated further before AC can be used for sediment remediation applications. Furthermore, there is an urgent need to investigate the effects of AC capping on oxygen and nutrients (i.e., nitrogen, phosphorus, silicon) availability, which may affect vital biogeochemical processes.

The overall goal of this study was to assess whether AC capping influences microbial activity and meiofaunal survival in marine sediments. This was assessed during a 4-week incubation experiment, where sediments collected in a contaminated harbor area (Oskarshamn, Baltic Sea) were exposed to two different powdered AC capping materials (from bitumen and coconut shells) and one capping control material (clay powder). The treated sediments were compared to non-capped control sediment cores. Micro-distribution of sediment oxygen and pH, fluxes of nutrients, along with meiofauna abundance and rates of key bacterial processes were quantified. This work aimed at filling important gaps in knowledge on the effects of powered AC on sediment geochemistry and microbial ecology, and to advance our knowledge on possible negative secondary effects during sediment remediation with AC.

## 2. Materials and methods

### 2.1. Sediment sampling and experimental design

Contaminated sediment was collected from the harbor area of Oskarshamn, south-east Sweden onboard of M/S Fyrbyggaren at a 15-m-deep station (57°15'52" N; 16°29' E) in May 2017. The site, which is located in a 16-m-deep trench located right outside the harbor entrance, has been described earlier as containing elevated concentrations of metals, PCBs and PAHs (Björinger, 2012). The contamination stems from past point sources, including a battery factory, a copper refinery, shipyards, and communal sewage. The benthic community of this site is dominated by chironomids, the polychaete *Hediste diversicolor* and a few tolerant mollusk species, typical of a low-biodiversity disturbed community. The harbor is a source of metals (zinc, copper, lead, arsenic, cadmium and cobalt), PCBs, and dioxins into the Baltic Proper (Tobiasson and Andersson, 2013). Currently, 500,000 m<sup>3</sup> of contaminated harbor sediments are dredged from the inner harbor with the aim to decrease transport of contaminants from the harbor to the Baltic Sea (Fathollahzadeh et al., 2015).

The sediment was collected using a modified box corer (Jonasson and Olausson, 1966). Box cores with intact sediment were sub-sampled on deck by inserting transparent plastic tubes ( $n = 27$ ; inner diameter = 4.6 cm; length = 30 cm) directly into the box core and retrieving them half filled with undisturbed sediment and half with *in situ* bottom water. *In situ* temperature was 9 °C, salinity was 7.1 and dissolved oxygen (O<sub>2</sub>) saturation was 95%, corresponding to ~340 μM O<sub>2</sub>. Additional bottom water was collected using a 20-L Niskin water sampler. Samples were then transported to Stockholm University at *in situ* temperature, where they were processed within 16 h after collection.

In the lab the sediment cores were placed in a 30-L incubation tank filled with bottom water. Aquarium pumps and air stones were

added to the tank to keep the solute distribution in the water overlying the sediment cores homogeneous and to maintain the water fully oxygenated. One sediment core was sliced at 0.5 cm intervals and sediment samples analyzed for water content, porosity, and organic matter content (loss on ignition, LOI). Additionally, the top 1-cm slice was centrifuged and the supernatant filtered and frozen for porewater ammonium concentrations (Bonaglia et al., 2014a). The sediment cores were subsequently pre-incubated in the dark and at constant temperature (9 °C) for five days. Approximately 30% of the water inside the water tank was replaced by *in situ* water twice a week to avoid excess buildup of waste-products from the benthic metabolism. Following sediment capping (section 2.2), the experiment was run for 28 days. To test for the short-term effect of capping on sediment metabolism, sediment microprofiling for O<sub>2</sub> and pH distribution were performed repeatedly during the experiment (section 2.3), and whole core incubations were used to determine solute fluxes (section 2.4) (Table 1). Two days before termination of the experiment, a whole core incubation experiment with addition of <sup>15</sup>N-nitrate was performed to determine nitrate reduction rates (section 2.5) (Table 1). The experiment was terminated and sediments from each replicate were sieved and preserved for the analyses of meiofaunal community structure (section 2.6) (Table 1).

## 2.2. Capping materials and application to the sediment

Thin-layer sediment capping was performed using two AC materials from Jacobi Carbons AB (Kalmar, Sweden). The first material consisted of bituminous coal-based powdered AC (AquaSorb BP2 PAC-S), while the second was powdered AC made of coconut shells (AquaSorb CP2 PAC-S). Both AC materials had the same particle size range ( $D_{50} = 15\text{--}35\text{ }\mu\text{m}$ ) and their efficiency to bind POPs has been previously demonstrated (Amstaetter et al., 2012). A third material, clay, was used as a control for the effect of sediment capping. This natural non-polluted sediment clay was collected from an offshore station in the Baltic Proper. Average clay particle size was comparable to the size of the AC particles. Each material was weighed (2.5 g), pre-wetted, and added to each of six replicate sediment cores, resulting in a cap of AC or clay with a dose of  $1.5\text{ kg m}^{-2}$  and a thickness of 4–6 mm, values comparable to previous thin-layer capping efforts (Abel et al., 2017; Cornelissen et al., 2012). Following the amendments, the sediment cores ( $n = 24$ ) were thus

allocated to four treatments, i.e., (1) the bituminous-based AC treatment (AC-B); (2) the coconut-based AC treatment (AC-C); (3) the clay treatment (CLAY); (4) the control treatment without capping (CTRL).

Structure and elemental composition of the three capping materials used for sediment capping were investigated by high resolution scanning electron microscopy (SEM, Jeol JSM 7000F) equipped with an Energy Dispersive X-ray Spectrometer (EDS, Oxford Instruments). Both secondary and backscattered electron images, and X-ray spectra were recorded using an accelerating voltage of 15 kV and working distance of 10 mm. The X-ray spectra analyses were performed using the INCA program package (Oxford Instruments, Buckinghamshire, UK). Briefly, an aliquot of the capping materials was pelletized to render the surface smooth. A site of interest of  $2.5 \times 2.5\text{ mm}$  was randomly selected and 12 spectra ( $\sim 600\text{ }\mu\text{m} \times 600\text{ }\mu\text{m}$ ) were analyzed for elemental composition.

## 2.3. Sediment O<sub>2</sub> and pH profiling and diffusive oxygen uptake

Sediment profiles of O<sub>2</sub> and pH were measured in two randomly selected sediment cores from each treatment (Revsbech, 1989; Revsbech and Jorgensen, 1986). Each sediment core was transferred to a temperature-controlled aquarium. Microprofiles were measured by mounting single sensors on a computer-controlled microprofiling unit (Unisense, Denmark). Oxygen was measured at a depth resolution of 200  $\mu\text{m}$  and pH at a resolution of 400  $\mu\text{m}$ . During the measurements the overlying water was gently circulated with an air stone to ensure the establishment of a steady diffusive boundary layer (DBL) on the sediment surface. Oxygen penetration depth (OPD) was defined as the distance between the sediment-water interface and the depth of onset anoxia (O<sub>2</sub> < 1  $\mu\text{M}$ ). Diffusive oxygen uptake (DOU) of the sediment was calculated from the oxygen depth profiles using Fick's first law corrected for the sediment porosity:

$$\text{DOU} = \phi \text{ Ds } d[\text{O}_2]/dx$$

where  $\phi$  is the porosity of the sediment, Ds is the molecular diffusion coefficient for O<sub>2</sub> in the sediment, and  $d[\text{O}_2]/dx$  indicates the variation of O<sub>2</sub> concentration with depth in the linear interval below the sediment-water interface. Sediment porosity (vol/vol)

**Table 1**

Summary of the endpoints tested and relative statistical test results. One-way parametric (*F* values) and non-parametric Kruskal-Wallis analysis of variance (*H* value) among the different treatments. Pair-wise comparison was performed by means of Tukey test. Differences between treatments: Different letters represent significant differences ( $p < 0.05$ ), while the same letter represents no significant differences ( $p > 0.05$ ) among treatments.

Parameter	Day	Analysis	p value	Differences between treatments			
				AC-B	AC-C	CLAY	CTRL
O <sub>2</sub> penetration depth	1	$F_{3,12} = 9.487$	0.002	a	a, b	b	b
O <sub>2</sub> penetration depth	24	$F_{3,12} = 2.835$	0.083				
NH <sub>4</sub> <sup>+</sup> flux	25	$F_{3,20} = 0.687$	0.571				
NO <sub>3</sub> <sup>-</sup> flux	25	$F_{3,20} = 14.001$	<0.001	a, b	a	b, c	c
PO <sub>4</sub> <sup>3-</sup> flux	25	$H_{3,20} = 15.140$	0.002	a	a, b	b	b
H <sub>2</sub> SiO <sub>4</sub> flux	25	$F_{3,20} = 3.228$	0.044	a, b	a	a, b	b
Total O <sub>2</sub> uptake	1	$F_{3,20} = 1.986$	0.149				
Total O <sub>2</sub> uptake	25	$F_{3,20} = 8.994$	<0.001	a	a	a, b	b
Diffusive O <sub>2</sub> uptake	1	$F_{3,12} = 17.278$	<0.001	a	a	b	b
Diffusive O <sub>2</sub> uptake	25	$F_{3,12} = 4.228$	0.030	a	a, b	a, b	b
Denitrification rate	26	$F_{3,20} = 32.201$	<0.001	a	a	b	b
D <sub>n</sub>	26	$F_{3,20} = 31.821$	<0.001	a	a	b	b
D <sub>w</sub>	26	$F_{3,20} = 13.407$	<0.001	a, b	a	b, c	c
DNRA rate	26	$F_{3,20} = 7.950$	0.001	a, b	a	b, c	c
Meiofauna abundances	28	$F_{3,16} = 10.331$	<0.001	a, b	a	b, c	c

was determined from density and water content of 5-mm-thick sediment slices. The molecular diffusion coefficient of  $O_2$  in the sediment, was calculated from the diffusion coefficient in the water corrected for tortuosity ( $1 - 2\ln(\phi)$ ). The molecular diffusion coefficient in the water was calculated for the specific temperature (9 °C) and salinity (7.1) of the incubations using the Marelac utility package developed in R (Soetaert et al., 2010), which is based on the equations presented in Boudreau (1997).

#### 2.4. Sediment core incubation for solute fluxes

A series of core incubation experiments were carried out to test the effect of sediment capping by AC on solute fluxes at the sediment-water interface. The incubation procedure followed the protocol of Bonaglia et al. (2017). Briefly, sediment cores ( $n = 24$ ) received teflon-coated stirring devices to ensure a well-mixed water column and a stable DBL during incubations. The cores were then sealed with rubber stoppers while avoiding trapping of gas bubbles in the water phase. Samples for  $O_2$  and nutrients were collected at the incubation start and end (incubation time 8 h). Concentrations of  $O_2$  were measured directly in each microcosm using a microsensor. Samples for dissolved nutrients i.e., ammonium ( $NH_4^+$ ), nitrate/nitrite ( $NO_x = NO_3^- + NO_2^-$ ), phosphate ( $PO_4^{3-}$ ) and silica ( $H_2SiO_4$ ) were immediately filtered using 0.2  $\mu m$  polyethersulfone (PES) filters. Concentrations of nutrients were determined with colorimetric analysis on a segmented flow nutrient analyzer system (OI Analytical, Flow Solution IV).

#### 2.5. Sediment core incubation for nitrate reduction pathways

Following the flux incubation, a second sediment core incubation experiment was carried out to determine rates of denitrification and dissimilatory nitrate reduction to ammonium (DNRA) according to the isotope pairing technique (IPT) (Nielsen, 1992). Briefly, 200 mL of a 9 mM  $^{15}NO_3^-$  (99.4  $^{15}N$  atom %) solution was added to the tank's water to reach a concentration of ca. 40  $\mu M$   $^{15}NO_3^-$ . Triplicate water samples were collected from the tank before and after addition of  $NO_3^-$ , filtered (PES, 0.2  $\mu m$ ), and refrigerated for later analysis to calculate  $^{15}NO_3^-$  enrichment (see below).

Sediment cores were pre-incubated uncapped overnight (ca. 8 h) to establish a linear production of  $^{29}N_2$  and  $^{30}N_2$  in the sediment (Dalsgaard et al., 2000). Two cores were sacrificed to measure background concentrations of  $^{29}N_2$  and  $^{30}N_2$ , while the remaining cores ( $n = 24$ ) were capped with butyl-rubber stoppers while avoiding bubbles and incubated with stirring for 8 h. The incubation was terminated by uncapping the cores, and gently mixing water and sediment in each core to slurry. A plastic syringe with a 10-cm-long tubing was used to sample ~20 mL slurry, which was allowed to overflow in a 12-mL Exetainer. The sample was immediately poisoned with 200  $\mu L$  of a 37% formaldehyde solution for later analysis of  $^{29}N_2$  and  $^{30}N_2$ .

An additional poisoned slurry sample (~10 mL) was sampled, dosed with 1 g KCl (1.3 M), shaken for 30 min, centrifuged at 3000 rpm for 10 min, filtered, and frozen at  $-20^\circ C$ . This sample was used for analysis of the  $^{15}NH_4^+$  fraction in the ammonium pool after conversion of  $^{15}NH_4^+$  to  $^{30}N_2$  using hypobromite in Exetainer vials (Warembourg, 1993). The concentrations of  $^{29}N_2$  and  $^{30}N_2$  were determined by gas chromatography-isotope ratio mass spectrometry (GC-IRMS) injecting headspace samples manually (Bonaglia et al., 2014a; Dalsgaard et al., 2000).

#### 2.6. Analyses of meiofauna

Following the two incubation experiments, all sediment cores were sieved sequentially through 1000 and 40  $\mu m$  sieves to retrieve macrofauna and meiofauna, respectively. The 40- $\mu m$  sediment fraction was preserved in 4% buffered formaldehyde and the meiofauna extracted by density extraction using a Levasil Colloidal Silica (AkzoNobel N.V.) solution with a density of  $1.21 \text{ kg dm}^{-3}$  (Bonaglia et al., 2014b). Briefly, each 40- $\mu m$  fraction was left in an Erlenmeyer flask with Levasil solution for 5 min. The top part of the solution containing meiofauna was decanted and washed with seawater. This extraction procedure was repeated twice and was followed by a third extraction that lasted 20 min. The extracts were sorted to count and classify meiofauna to the group level using a binocular stereo microscope (Leica M80) at  $60\times$  magnification.

#### 2.7. Calculations and statistical analyses

Total oxygen uptake (TOU) and fluxes of nutrients ( $NH_4^+$ ,  $NO_x^-$ ,  $PO_4^{3-}$ ,  $H_2SiO_4$ ) between sediment and water phases were calculated from the difference in water concentrations at the beginning and end of the incubation, accounting for the varying volume of incubated water. In a similar fashion, excess  $^{29}N_2$  and  $^{30}N_2$  determined by GC-IRMS were used to calculate the  $N_2$  production over time and the associated denitrification rate (D14) (Nielsen, 1992). Based on the measured concentrations of endogenous  $^{14}NO_3^-$  and exogenous  $^{15}NO_3^-$ , and on the equations reported by Nielsen (1992), the denitrification rate could be distinguished between denitrification fueled by water column  $NO_3^-$  ( $D_w$ ) and from denitrification coupled to nitrification ( $D_n$ ). Rates of DNRA were calculated based on  $^{15}NH_4^+$  production over time, following the rationale of Risgaard-Petersen and Rysgaard (1995).

Differences in OPD, nutrient fluxes, TOU, DOU, rates of nitrate reduction and meiofauna abundances among the four treatments (AC-B, AC-C, CLAY and CTRL) were tested using one way analysis of variance (ANOVA) (Table 1). When datasets were not normally distributed, even after data transformation ( $\log(x+1)$ ), one way ANOVA on ranks (Kruskal-Wallis test) was performed instead. Post-hoc pairwise multiple comparisons (Tukey test) were performed to identify which treatments significantly differed from others. A two-way ANOVA with treatment and meiofaunal taxa as factors was performed for testing differences in meiofaunal abundances. Statistical analyses were performed using SigmaPlot for Windows, version 13.0 (Systat Software). Principal coordinates analysis (PCoA) was performed with R software, version 3.4.3. If not otherwise stated, measurements are reported in the results as mean  $\pm$  standard error of the mean (sem).

### 3. Results

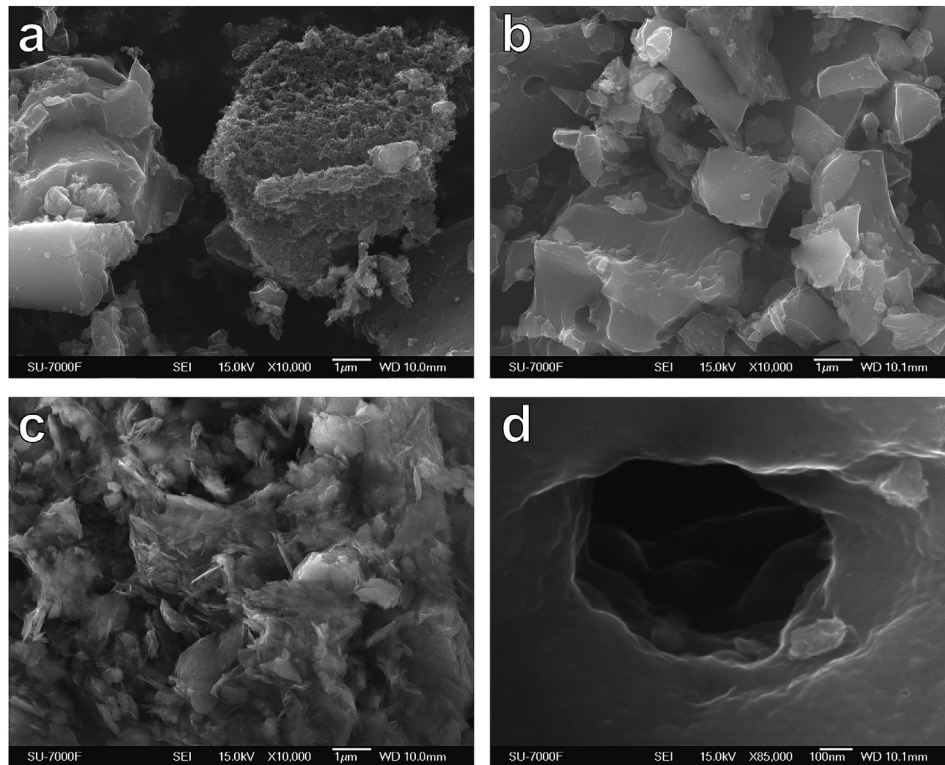
#### 3.1. Experimental features

##### 3.1.1. Material characteristics

Images from the SEM revealed that the two AC materials presented both nanometer-sized and micrometer-sized pores (Fig. 1a and Fig. 1b). The coconut-based AC (AC-C) has smoother surfaces whereas the bitumen-based AC (AC-B) has more fragmented surfaces with featured pores in the nanometer scale and thus potentially a larger surface-to-volume ratio (Fig. 1). The clay material had a different structure and was characterized by randomly oriented exfoliated sheets, often resulting in pointy sharps, while pores could not be detected (Fig. 1c).

Elemental composition of the two AC materials was similar, and was dominated by C (mean 87–89%), O (9–10%), Si (0.1–1.1%) and Ca (0.1–0.6%) (Suppl. Tables 1 and 2). However, AC-B (AquaSorb





**Fig. 1.** Scanning electron microscope images of (a) activated carbon powder prepared from bitumen (AC-B); (b, d) activated carbon powder from coconut shell (AC-C); (c) clay powder used as a control, inactive capping material (CLAY). Micrographs were taken at a magnification of  $\times 10,000$  to illustrate the powder structure (a, b, c), and of  $\times 85,000$  to illustrate the structure of a pore in the coconut-based activated carbon material (d).

BP2) contained considerable amounts of Al (0.7%) and S (0.7%), elements that were not found in AC-C. AC-C (AquaSorb CP2) contained K (1.1%), which was not present in AC-B. The elemental composition of clay was substantially different than those of the AC materials (Suppl. Table 3). The most abundant elements present in the clay material were O (55%), Si (24%), Al (8%), Fe (4%) and K (3%). Other minor elements ( $\leq 2\%$ ) included Na, Mg, S, Ca and Ti.

### 3.1.2. Sediment properties, pH and $O_2$ microprofiles

The sediment used for profiling and incubation was the 0–13 cm depth layer of Oskarshamn harbor sediment. This sediment had an average organic carbon content of 18.1% (LOI), water content of 83.8%, and porosity of 0.85. Porewater  $NH_4^+$  concentration in the top

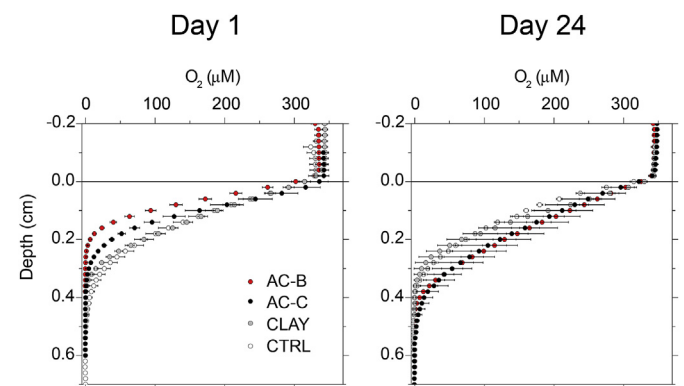
1-cm sediment layer was  $151 \mu M$ . *In situ* bottom water nutrient concentrations were  $2.2 \mu M NH_4^+$ ,  $2.4 \mu M NO_3^-$ ,  $0.8 \mu M PO_4^{3-}$ , and  $54.9 \mu M H_2SiO_4$ .

Oxygen concentration microprofiles showed that  $O_2$  was always consumed and not produced in the sediment, and that total  $O_2$  respiration was confined to a  $<0.5$ -mm-thick layer below the water-sediment interface (Fig. 2). At the beginning of the experiment (one day after the capping), oxygen penetration depth (OPD) in CTRL was  $0.42 \pm 0.04$  cm and it was reduced to  $0.26 \pm 0.00$ ,  $0.35 \pm 0.02$  and  $0.40 \pm 0.00$  cm in AC-B, AC-C and CLAY, respectively (Fig. 2). OPD in AC-B was significantly lower than in CLAY and CTRL ( $p = 0.002$ ; Table 1). After 24 days of exposure to the capping materials, OPD was higher in the AC treatments, being  $0.42 \pm 0.02$  and

**Table 2**

Abundances of most common meiofaunal taxa and of total meiofauna. Abundances ( $ind.10^{-3} m^{-2}$ ) are expressed as average (avg) with relative standard error of the mean (sem),  $n = 5$  per treatment.

	AC-B		AC-C		CLAY		CTRL	
	avg	sem	avg	sem	avg	sem	avg	sem
Nematoda	26	5	24	5	34	9	71	7
Harpacticoida	6	3	9	2	20	9	18	5
Harpacticoida nauplii	0	0	0	0	1	1	4	2
Other copepods	0	0	0	0	0	0	2	1
Turbellaria	14	4	13	3	37	5	46	10
Foraminifera	16	1	14	3	41	6	49	9
Ostracoda	13	3	8	1	20	5	22	6
Rotifera	13	4	15	6	25	6	15	5
Halacaroida	3	1	0	0	2	1	4	1
Oligochaeta	4	1	4	1	5	2	7	2
Others	0	0	1	1	1	1	2	1
<b>Total meiofauna</b>	<b>97</b>	<b>18</b>	<b>90</b>	<b>15</b>	<b>186</b>	<b>19</b>	<b>241</b>	<b>34</b>



**Fig. 2.** Distribution of  $O_2$  concentrations (means  $\pm$  sem,  $n = 6$ ) in sediments capped with bituminous AC (AC-B) and sediments capped with coconut shell AC (AC-C), in sediments capped with clay (CLAY) in control uncapped sediments (CTRL). Oxygen profiles were determined 1 day and 24 days after sediment capping.

$0.46 \pm 0.05$  cm in AC-B and AC-C, respectively, compared to CLAY and CTRL, which had OPDs of  $0.33 \pm 0.04$  and  $0.39 \pm 0.01$  cm, respectively (Fig. 2). This last difference, however, was not statistically significant ( $p > 0.05$ ; Table 1).

At the beginning of the experiment (day 1), microprofiles of pH in CTRL and CLAY showed that pH decreased sharply downward through the sediment-water interface reaching a minimum (pH 7–7.5) between 0.5 and 1 cm, and increased with depth below this layer to stabilize at 7.5–7.8 below 1.5 cm depth (Fig. 3). The pH profiles in AC-amended sediments displayed an opposite pattern, where pH increased in the first 1.5 cm below the sediment-water interface, reaching maximum at 0.3–0.4 cm depth (pH 9.7 and 9.0 for AC-B and AC-C, respectively) (Fig. 3). With a 0.4–0.6 cm capping layer, it results that the pH peaked in the middle of the AC cap. After 7 days, the initially observed pH trends were still apparent, although less pronounced: CTRL and CLAY had a subsurface pH minimum (pH 7) followed by a steady increase and stabilized at pH 7.5, while AC-B and AC-C had an evident subsurface pH maximum (pH 8.5–8.9) followed by a decrease and stabilization at pH 7.8 (Fig. 3). The pH profiles in CTRL and CLAY did not change between 7 and 14 days after experiment start, while in the active cap layers the pH peak decreased to pH 8.1 and 8.4, in AC-B and AC-C, respectively (Fig. 3). After 24 days of exposure, CTRL, CLAY and AC-B pH profiles all had a very similar shape, while AC-C maintained a relatively high (pH 8.2) and constant value from the water down to 0.6 cm sediment depth, and showed a minimum (pH 7) at 1 cm depth (Fig. 3).

### 3.2. Effects on nutrient and oxygen fluxes

After 25 days of exposure to the capping materials, differences in dissolved nutrient fluxes among treatments were statistically significant ( $p < 0.05$ ; Table 1) with the exception of ammonium fluxes, which showed too much variability among replicates to result significant ( $p > 0.05$ ; Table 1, Fig. 4). Fluxes of nitrate-nitrite sum were 45 and 53% lower in AC-B and AC-C, respectively, than in CTRL ( $p < 0.001$ ; Table 1, Fig. 4), while fluxes in CLAY were 20% lower than in CTRL but this difference was not significant ( $p > 0.05$ ; Table 1, Fig. 4). Efflux of phosphate was 91% lower in AC-B, 66% lower in AC-C and 19% higher in CLAY compared to CTRL (Fig. 4), resulting in significant differences between AC-B compared to CTRL and CLAY ( $p = 0.002$ ; Table 1, Fig. 4). Silicate fluxes were lowest in AC-C, resulting in a 73% reduction compared to CTRL ( $p = 0.04$ ; Table 1, Fig. 4). Fluxes of silicate in AC-B and CLAY were also reduced

(43 and 32%, respectively) but not significantly ( $p > 0.05$ ; Table 1, Fig. 4).

The day after capping (day 1), total oxygen uptake (TOU) was not significantly different among treatments ( $p > 0.05$ ; Table 1; Fig. 4). However, after 25 days of exposure to the capping materials, TOU was significantly lower in both AC-B (30% reduction) and AC-C (43% reduction) treatments compared to CTRL (Table 1, Fig. 4). CLAY, although causing a 20% reduction, did not significantly affect total oxygen demand ( $p > 0.05$ ; Table 1; Fig. 4). At day 1, diffusive oxygen uptake (DOU) differed significantly among treatments ( $p < 0.001$ , Table 1) and was 70% and 46% higher in the AC-B and AC-C, respectively, than in CTRL (Fig. 4). At day 25, the trend was reversed and DOU became significantly lower (44% reduction) in AC-B compared to CTRL ( $p = 0.03$ ; Table 1, Fig. 4), while AC-C and CLAY (30 and 33% reduction, respectively) did not result in significant changes ( $p > 0.05$ ; Table 1, Fig. 4).

### 3.3. Effects on nitrate reduction pathways

After 26 days of exposure to the capping materials, rates of total denitrification, denitrification coupled to nitrification ( $D_n$ ), denitrification of nitrate diffusing from the water column into the sediment ( $D_w$ ) and dissimilatory nitrate reduction to ammonium (DNRA) were significantly different among treatments ( $p < 0.05$ ; Table 1). Denitrification and  $D_n$  rates were approximately three times lower in AC-B (63% reduction) and AC-C (62% reduction) compared to CTRL (Fig. 5), resulting in significant differences between AC-B and AC-C compared to CLAY and CTRL ( $p < 0.001$ ; Table 1). Rates of DNRA were significantly lower in AC-B (66% reduction) and AC-C (87% reduction) compared to CTRL ( $p < 0.001$ ; Table 1). CLAY did not induce any significant change in nitrate reduction pathways compared to CTRL ( $p > 0.05$ ; Table 1). In all treatments, denitrification was almost exclusively (97–98%) sustained by  $D_n$ , while  $D_w$  was negligible.

### 3.4. Effects on meiofaunal communities

At the end of the experiment (day 28), meiofauna abundance was significantly reduced in the two AC treatments (60–62% reduction) compared to untreated sediment ( $p < 0.001$ ; Tables 1 and 2). CLAY (20% reduction) did not result in any significant change in meiofauna abundances compared to CTRL ( $p > 0.05$ ; Table 1). The most affected taxa were Nematoda, Turbellaria and Foraminifera, whose abundances were significantly lower in the

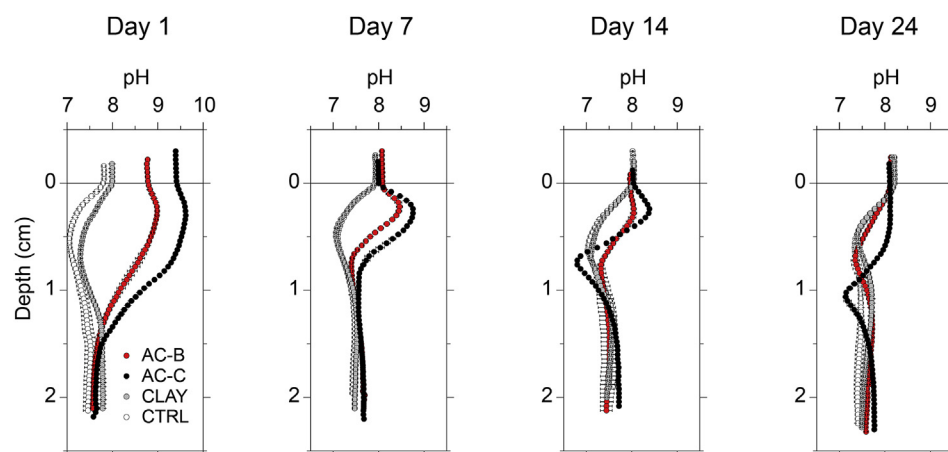
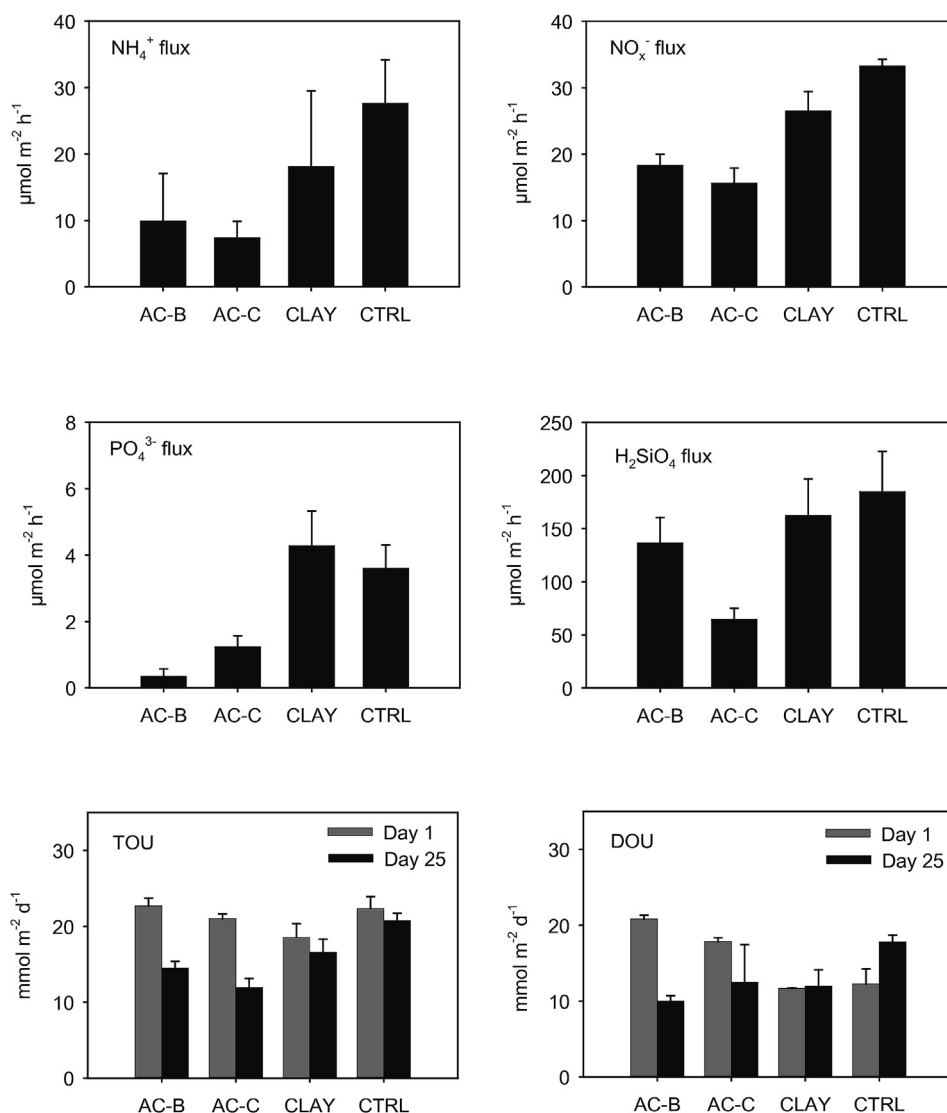


Fig. 3. Distribution of pH (means  $\pm$  sem,  $n = 6$ ) in sediments capped with bituminous AC (AC-B) and sediments capped with coconut shell AC (AC-C), in sediments capped with clay (CLAY) in control uncapped sediments (CTRL) at different times after sediment capping.



**Fig. 4.** Net fluxes of ammonium (NH<sub>4</sub><sup>+</sup>), nitrate + nitrite (NO<sub>x</sub><sup>-</sup>), phosphate (PO<sub>4</sub><sup>3-</sup>), dissolved silica (H<sub>2</sub>SiO<sub>4</sub>), total oxygen uptake (TOU) and diffusive oxygen uptake (DOU) measured in sediment cores 1 day (black bars) and 25 days (gray bars) after sediment capping. Bars represent mean values ± sem, n = 24. Note that TOU and DOU values are reported in absolute values (all sediments had net negative oxygen fluxes). AC-B = sediments capped with bituminous AC; AC-C = sediments capped with coconut shell AC; CLAY = sediments capped with clay; CTRL = control uncapped sediments.

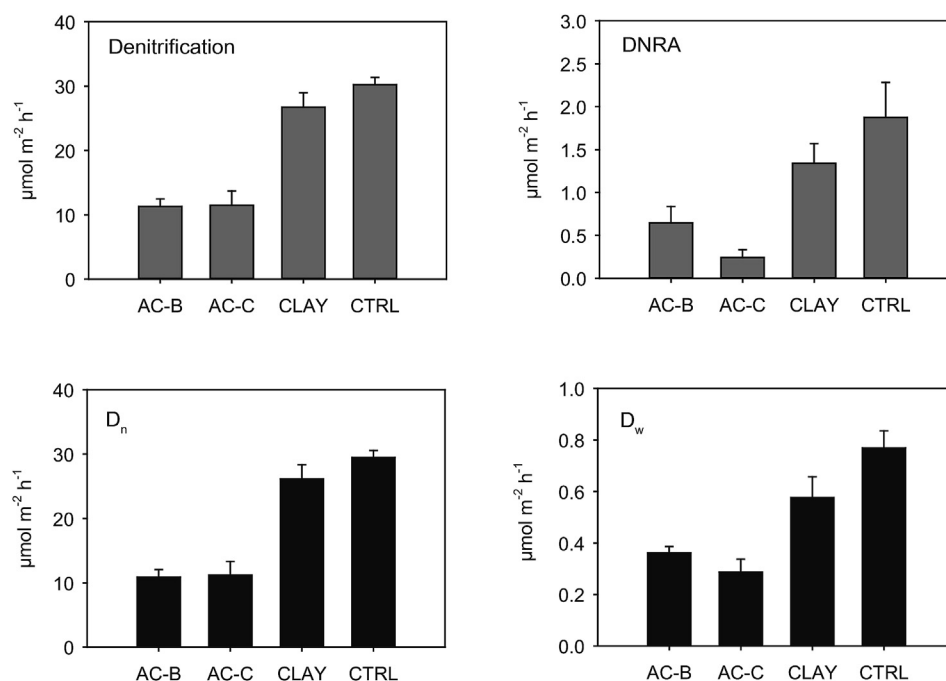
two AC treatments compared to CTRL (two-way ANOVA,  $p < 0.001$ ; Suppl. Table 4). Harpacticoida (copepods) abundances were significantly lower in AC-B than in CTRL (two-way ANOVA,  $p < 0.001$ ; Suppl. Table 4). Results of the two-way ANOVA also showed that abundances of Rotifera and Ostracoda were not significantly affected by AC amendments ( $p > 0.05$ ; Suppl. Table 4). In addition, the PCoA of meiofauna community composition showed that CTRL and CLAY cluster differently than the two AC treatments (Fig. 6), further indicating that AC affected meiofauna community structure.

#### 4. Discussion

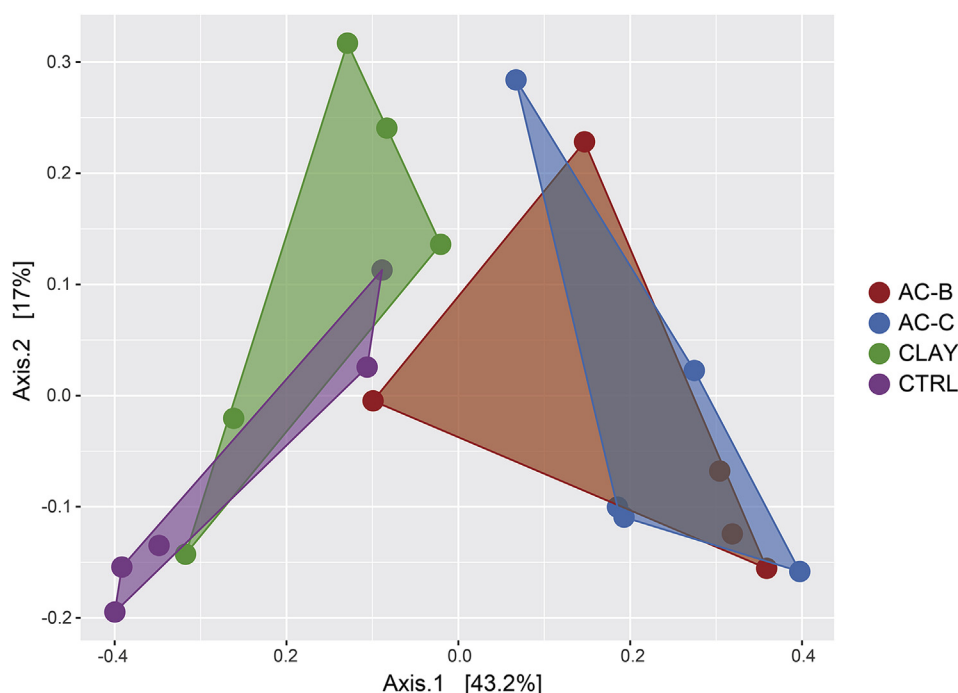
This study assessed chemical and biological effects of activated carbon (AC) amendment applied to contaminated sediments as a thin-layer cap. Results from sediment core incubation experiments showed that AC capping had a significant impact on the main nitrate reduction pathways, i.e., denitrification and dissimilatory reduction to ammonium (DNRA). These two processes were

reduced by 63 and 66%, respectively, in presence of bituminous coal-based AC (AC-B), and by 62 and 87%, respectively, in presence of coconut shell-based AC (AC-C). The drastic decline in coupling between nitrification and denitrification was the main cause for the decrease in denitrification activity, suggesting a shortage in the supply of nitrate to denitrification. The overall reduction in nitrate effluxes at the sediment water interface in spite of the decrease in the main nitrate removal processes in the sediment (i.e., denitrification and DNRA) further indicates that nitrification activity was inhibited by AC capping.

Together with pH, oxygen and ammonium concentrations are considered the most critical environmental factors controlling nitrification activity in aquatic systems (Canfield et al., 2005). Our experiments show that dissolved oxygen concentrations did not significantly differ between treatments, and that the same was true for ammonium fluxes. However, AC materials had a strong effect on pH. In particular, pH in the oxic sediment layer, where nitrifiers are active, increased to 9.0 in AC-B and 9.7 in AC-C one day after capping; to 8.5 in AC-B and 8.9 in AC-C one week after capping; and



**Fig. 5.** Rates of nitrate reduction processes measured in sediment cores incubated with the addition of  $^{15}\text{NO}_3^-$  26 days after sediment capping. Bars represent mean values  $\pm$  sem,  $n = 24$ . AC-B = sediments capped with bituminous AC; AC-C = sediments capped with coconut shell AC; CLAY = sediments capped with clay; CTRL = control uncapped sediments.



**Fig. 6.** Principal Coordinates Analysis (PCoA) based on the abundance of each meiofaunal taxa for the four treatments. AC-B = sediments capped with bituminous AC; AC-C = sediments capped with coconut shell AC; CLAY = sediments capped with clay; CTRL = control uncapped sediments.

to 7.9 in AC-B and 8.2 in AC-C at the end of the experiment. This corresponds to an increase of up to 2.7 pH units in the nitrification zone compared to uncapped or clay-capped sediments, which had a pH range of 7–7.5 throughout the experiment. This increase in pH could be explained by leaching of alkaline compounds from the AC ash and/or development of alkaline surface oxides and hydroxides produced upon thermal activation of the two carbonaceous

materials (Mohan and Pittman Jr., 2006). Also, the larger pH increase from AC-C capping compared to AC-B capping is consistent with the higher content of alkaline compounds, like potassium oxyhydroxides, in AC-C shown in the elemental composition analysis.

In aquatic sediment, nitrification is strongly influenced by pH and maximum rates have been demonstrated to occur at pH around 7.5 (Strauss et al., 2002). In activated-sludge systems, pH optimum



for nitrification activity ranges between 7.0 and 8.0 (Antoniou et al., 1990; Jones and Paskins, 1982; Painter and Loveless, 1983). *Nitrosomonas*, one of the most naturally abundant ammonium oxidizers ( $\text{NH}_4^+ \rightarrow \text{NO}_2^-$ ), displays maximum activity between pH 7.9 and 8.2, while *Nitrobacter*, a common nitrite oxidizer ( $\text{NO}_2^- \rightarrow \text{NO}_3^-$ ), exhibits a pH optimum between 7.2 and 7.6 (Alleman, 1985; Villaverde et al., 1997). In environments with high pH ( $\text{pH} \geq 8$ ) and where ammonium reaches high concentrations, a large fraction of the ammonium pool is present as free ammonia (Anthonisen et al., 1976; Ford et al., 1980). The high organic content of Oskarshamn sediments (18.1% LOI) led to high ammonium formation from organic matter mineralization, resulting in porewater ammonium concentrations of ca. 150  $\mu\text{M}$  in the top 1-cm sediment layer. These conditions have been shown to support an active and abundant population of nitrifiers (Canfield et al., 2005; Strauss et al., 2002). We suggest that high ammonium and pH conditions, such as those found in our AC-capped sediments, resulted in the inhibition of nitrification activity due to presence of free un-ionized ammonia. For example, at pH 8.5 and at ammonium concentrations of about 150  $\mu\text{M}$ , free ammonia reaches concentrations of ca. 50  $\mu\text{M}$  (Ford et al., 1980), which is toxic to nitrifying microorganisms and particularly to *Nitrobacter* (Anthonisen et al., 1976; Ford et al., 1980; Meiklejohn, 1954). This effect was evident in nitrate fluxes, which were halved in the presence of AC. The reduced supply of nitrate from nitrifiers may have caused the drastic decrease in nitrate reduction rates during the first two weeks after capping, i.e., when pH was highest in the two AC treatments.

Factors other than pH must explain the 62–87% decrease in nitrate reduction, as these rates were measured approximately four weeks after capping when pH conditions, at least in the AC-B treatment, had almost recovered. One of these factors may be that labile organic carbon became less available in contact with AC, which has a high density of surface sites and pores to maximize binding capacity for organic contaminants in sediments (Amstaetter et al., 2012; Ghosh et al., 2011). An undesired ecological side effect may thus arise in natural benthic systems due to the potential of AC to reduce not only the bioavailability of organic contaminants but also that of natural sedimentary organic compounds, such as nutritious amino, fatty and humic acids (Quinlivan et al., 2005; Schreiber et al., 2005; Velten et al., 2011). Quantification of bulk organic carbon is commonly used in sediment biogeochemistry but does not discriminate between labile and refractory pools, which makes it a poor indicator of bioavailable organic carbon (Arnosti and Holmer, 2003). Direct measurements, such as sediment oxygen uptake, have been shown to be better proxies for quantification of available substrates to microbial communities in sediments (Glud, 2008). By the end of our experiment, sediment oxygen uptake was 30–43% lower in the AC treatments compared to the control uncapped sediments. As the oxic zone was ca. 5-mm thick and the cap layer 4–6 mm, the lowered oxygen uptake was likely due to depletion of labile organic matter in the cap layer. Thus, we suggest that the aerobic heterotrophic bacteria and denitrifiers were starved from being forced to colonize an environment consisting of almost pure AC, with presumably extreme food scarcity.

In aquatic sediments denitrification and DNRA are strictly dependent on organic substrates as they are processes that are almost exclusively carried out by heterotrophic bacteria (Burgin and Hamilton, 2007; Giblin et al., 2013; Zumft, 1997). Organic compounds sorbed to soil or clay particles are generally available to heterotrophs due to weaker bonds (Crocker et al., 1995). Our results show that AC capping resulted in a 3-fold decrease in denitrification and up to an 8-fold reduction in DNRA, while clay capping did not have any significant effect on solute fluxes and microbial processes. The latter observation is in line with evidence from a

previous capping experiment (Näslund et al., 2012). Nutrient fluxes, in particular those that are biologically mediated, such as nitrate and silicate fluxes, showed similar trends, with both AC materials causing significantly lower effluxes than control sediment. However, AC is unlikely to have had a direct effect on nitrate and silicate concentrations, as AC has a low affinity for inorganic nutrients (Callaway and Aschehoug, 2000). Benthic phosphate fluxes deserve special attention as they are primarily regulated by sediment geochemistry rather than by biological activity. Phosphate efflux was significantly lowered by AC, although only the decrease measured in the AC-B was significant compared to the CTRL. The more effective reduction of phosphate efflux in the AC-B may be due to the different composition of the materials. The bituminous AC contained substantial amounts of Al, probably in different phases of Al-oxides and hydroxides, which have been shown to efficiently bind phosphate in brackish sediments (Rydin et al., 2017).

The majority of AC amendment tests in sediments that included biological endpoints have shown no effects on benthos (72% of studies), but some studies found either positive (10%) or negative secondary effects (18%) (Janssen and Beckingham, 2013). To date, studies on the ecological effects of AC capping have been limited almost exclusively to macrofauna studies. Meiofauna, despite being orders of magnitude more abundant and having a more diverse community structure than macrofauna, had only been considered in one toxicological study with AC known to the authors (Näslund et al., 2012). The study found that sediment capping with a dose of 1  $\text{kg m}^{-2}$  powdered AC from coconut shells (compared to our 1.5  $\text{kg m}^{-2}$  dose) did not produce significant effects on meiofaunal abundance and community structure (Näslund et al., 2012). The average abundance of nematodes, the most common meiofaunal taxon, was ~30% lower in presence of AC than in untreated controls, but their statistical analysis lacked power (Näslund et al., 2012). Our study showed that nematode populations were significantly reduced in presence of both AC-B (–64% abundance) and AC-C (–66%). The meiofauna community in Oskarshamn sediments likely does not represent an undisturbed sediment meiofauna community, because it has been pre-exposed to contaminant mixtures *in situ* (Stark et al., 2017). The benefit of reduced organic contaminant bioavailability by AC on our meiofaunal communities could not be seen here perhaps because recolonization by natural meiofauna communities was not possible in our enclosed chambers. Recent toxicity tests with benthic amphipods exposed to Oskarshamn harbor sediment showed a positive impact of AC amendment on survival and reproduction (Rämö, unpublished data). However, granular AC was used in those experiments.

The previously reported negative effects of AC on benthic macroinvertebrates include increased mortality, reduced growth, decreased lipid content, and alterations of animal behavior (Janssen and Beckingham, 2013). In our experiment, total meiofauna abundance was only 40% in AC-B and 38% in AC-C compared to CTRL. In comparison, clay amendment did not cause any significant mortality of meiofauna. Recent studies have shown that powdered activated carbon may be detrimental to benthic macrofauna as, upon ingestion, sharp AC particles may physically damage the gut microvilli of sediment deposit-feeders (Abel et al., 2017; Nybom et al., 2015, 2016). It is possible that this mechanism, i.e., decreased assimilation efficiency following damaged gut microvilli, was responsible for the increased meiofauna mortality found in our study. Most of the added AC particles were in the 15–35  $\mu\text{m}$  range and may have been ingested by large meiofauna. For examples, nematodes of the genus *Tripyloides* have been shown to ingest 40–80  $\mu\text{m}$  ciliates (Moens and Vincx, 1997). Our results thus strongly suggest that both of the fine powdered ACs used here also have impact on the resource acquisition and nutrition of

meiobenthos.

It has been shown that AC efficiently adsorbs nutritious organic compounds, such as humic and fulvic acids, carbohydrates, and proteins (Kilduff et al., 1996; Schreiber et al., 2005; Velten et al., 2011). A novel hypothesis is therefore that ingested AC particles may reduce the uptake of nutrients from organic matter dissolved in the gut of meiofauna during digestion. The fact that the small rotifers, which feed on particles of 0.5–18 µm (Brönmark and Hansson, 2017), were not affected by AC in our study, could support that either mechanical damages or sequestration of nutritious organic matter did not occur in these animals to the same extent as in larger meiofauna, such as nematodes, foraminifers, and ostracods, which could likely ingest larger fractions of the tested AC materials.

## 5. Conclusions

We show both structural and functional effects of thin-layer capping with two types of powdered AC and with clean sediment (clay) on microbial and meiofaunal benthic communities. AC amendment resulted in significant decreases of both biologically-mediated nutrient fluxes and rates of microbial processes, likely due to increased pH of the porewater caused by the alkaline composition of the AC materials and depletion of natural organic matter, which is required for the metabolism of most aerobic, denitrifying bacteria and meiofauna. Irrespective of the AC material used, this study suggests that sediment remediation with powdered AC may lead to harmful effects on microbial activity and meiofauna, which provide vital ecosystem functions to the aquatic environment. In contrast, thin-layer capping with clay did not harm microorganisms and meiofauna. However, powder AC capping significantly decreases contaminant fluxes from Oskarshamn sediments, while clay does not seem to be effective for remediation (Rämö, unpublished data). Considering the stronger effects on sediment geochemistry and microbial functions caused by the coconut-derived AC compared to the bituminous AC and clay, we recommend that sediment capping with aluminum-containing bituminous AC be performed in environments where internal phosphorus load represents an ecological problem in addition to organic contamination.

The functional effects described here are measured in more detail than in earlier studies, with clear biogeochemical explanatory mechanisms. However, our results describe the situation from several hours to four weeks after sediment capping with activated carbon was performed. At the end of the experiment, the impact of the bituminous AC cap on pH was already attenuated. We cannot exclude that deposition of fresh organic material on top of the AC layer would over time mitigate some of the observed effects in *in situ* remediation treatments. We thus recommend that similar measurements be repeated in long-term experiments. Further studies are needed to assess particle-size effects on meiofauna abundances, community structure and microbially-mediated ecosystem functions as larger particles may produce fewer and less severe effects on these endpoints. Meanwhile, we advise to restrict amendment with powdered AC to heavily contaminated sites, where the local sediment pollution is a significant threat to the ecosystem and where less invasive methods such as capping with clay or monitored natural recovery cannot be pursued due to high risk of contaminant spread.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.watres.2018.10.083>.

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